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Enhancement of light Naphtha quality using calcite adsorbent from eggshells by adsorptive desulfurization

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ABSTRACT

The presence of sulfur in transportation fuels has bad consequences for health and the environment, and there are many techniques used for removing or eliminating sulfur content, especially hydrodesulfurization. Hydrodesulfurization is the classical technique for desulfurization, but it is characterized by working at elevated temperatures and pressures as well as high costs. For this, there are many alternative methods, such as adsorptive, oxidative, extractive, and so on. The adsorptive desulfurization (ADS) is one of the most promising methods for sulfur reduction because of its ability to work under ambient conditions and ADS can significantly enhance the quality of light naphtha by reducing its sulfur content and improving its suitability for downstream processes such as catalyst poisoning and corrosion. The calcite prepared from eggshell was investigated here as an adsorbent for sulfur compounds from light naphtha. The adsorbent was characterized by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The investigation of adsorbent activity was done by batch adsorption, and the chosen studied variables are temperature, adsorbent dosage, and contact time with ranges of 20–40 C°, 1–3 g, and 15–45 min, respectively, which were designed according to the Box–Behnken experimental design and the experiment results were analyzed using Minitab software version 17. The results show that the sulfur-removing efficacy ranged between 45 and 60%, while optimum sulfur removal efficiency is 61% at the following operation conditions: 40 °C, 3 g, and 45 min for temperature, adsorbent dosage, and adsorption time respectively.

Adsorption isotherms Langmuir and Freundlich were examined, and the results show the Freundlich isotherm is more suitable to describe the adsorption of these sulfur compounds.

1. Introduction

The presence of sulfur organic compounds (SOCs) in crude oil may cause harmful effects due to their unfavorable environmental influences via sulfur oxide emissions, which cause acid rain as well as other bad human health consequences. Also, they result in the corrosion of the internal combustion engines, poisoning catalysts (Hussein and Fadhil 2021). The sulfur content of crude oil is expressed as a percentage of the total weight of the crude oil, which usually ranges from less than 0.1% to more than 5%. The four major groups can be classified into these compounds, namely sulfides, disulfides, mercaptans, and thiophenes (Kadhum and Albayati 2022). The emission standards, like European emission and Bharat Stage (BS) emission standards, have been framed to control the various pollutants, including sulfur emissions, to < 10 ppm in the fuel at present (Jha et al., 2020).

Now, the current industrial method for the removal of sulfur compounds from fuels is hydrodesulfurization (HDS), which is a high-temperature and high-pressure catalytic process. This makes HDS a very costly option for deep desulfurization (Srivastava 2012). There are several methods and approaches to sulfur removal from crude oil, like adsorptive desulfurization, extractive desulfurization, Oxidative desulfurization (ODS), and bio-desulfurization (BDS) (Mohammed et al., 2022). HDS is not efficient in the removal of aromatic refractory sulfur compounds such as thiophene derivatives (dibenzothiophene (DBT) and 4,6-dimethyl dibenzothiophene (DMDBT)), which are the least reactive and pose more danger to the environment (Saleh et al., 2016).

Adsorptive desulfurization (ADS) has several advantages over other methods, such as minimal operational requirements and low penalty fees for sulfur removal. One of the most important factors associated with the adsorption method is the choice of adsorbent, which eventually determines the efficiency, economics, and versatility of the process (Mohammad N Abbas and Alalwan 2019). There are many materials

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used as adsorbents for ADS, such as charcoal-granular activated carbon (Bakr and Salem 1994), magnetite nanoparticle-loaded bentonite (Ishaq et al., 2017), activated alumina (Srivastav and Srivastava 2009), activated carbon (AC) (Chen et al., 2020),modified activated carbon with nickel and copper (Naife and Finish 2021), the non-ionic liquid silica gel adsorbent (Kundu and Mitra 2022b)etc.

. Calcium carbonate ($CaCO_3$) is an abundant material in nature and is widely used by animals for shell and exoskeleton formation. Calcite is the most stable polymorph of calcium carbonate at normal conditions, so it was used broadly to study complex chemical and physical phenomena that may equally affect other mineral and chemical compound systems (Ataman et al., 2016). Eggshell may be one of the most important sources for calcite, so it has been studied as a potential adsorbent for certain heavy metals and organic compounds due to its suitable porosity, which makes it an attractive adsorbent (Elkady et al., 2011). One of the benefits of using eggshells as adsorbents is that they are easily renewable, regenerated, affordable, biocompatible, environmentally friendly, and very stable in organic solvents (Sembiring et al., 2021a).

Abbas and Ibrahim used white eggshell as adsorbent Catalytic desulfurization from light naphtha under following operation conditions; H_2O_2/light naphtha ration is 4, pH equal 1, agitation speed equal 400 rpm, and batch time equal 150 min . The best sulfur removal efficiency is 56.78%, (Mohammmed Nsaif Abbas and Ibrahimm 2020a) for that it was suggest to use calcite adsorbent prepared from eggshell and activated with HCl solution. Thus, in this work, adsorptive desulfurization of light naphtha supplied from the Ad-Diwaniya refinery with a sulfur concentration of 776 ppm by using calcite ($CaCO_3$) absorbent prepared from eggshell as an adsorbent for (ADS). The study consists the investigation of the impact of several operating conditions on desulfurization efficiency; temperature, weight of the adsorbent, and contact time where these variables are arranged according to Box-Behenken experimental design . This work gives new information about the light naphtha desulfurization process. It shows how calcite can be used as an adsorbent to remove about 60% of the initial sulfur content.

2. Experimental work

Chickens Eggshells were collected from homes, restaurants, and hatcheries in large quantities to extract an adsorbent from them. Hydrochloric acid HCl (CHD company: 36.5%) and deionized water DW (produce in the lab), while the feedstock is light naphtha supplied from Al-Diwaniya refinery with sulfur content (776 ppm) as one of the atmospheric distillation fractions, it is listed in Table 1, which was tested in Al-Diwaniya refinery/Ministry of Oil.

The equipment used in this work is a magnetic hot plate (Alfa Company, speed range 100–1800 rpm with a temperature range of 30–300 °C), a drying oven (Heraeus Company, maximum temperature 220 °C), a digital electronic balance (maximum weight 220 g with 0.0001 g accuracy), a pH meter (HANNA Instruments), an industrial grinder, a 200-mesh sieve, and some other class laboratory equipment.

Adsorbent calcite is prepared from chicken eggshells by activation and heating methods as follows: washing the chicken eggshells with water until they are very clean. Then they were dried in the sun, then mashed with a pestle and mortar. They were sieved to obtain a grain size that passes a 200-mesh sieve. Then, they were heated in an oven for 15 min at 110 °C, then activated with a 0.1 M HCl solution for two days, then filtered and washed by using distillation water until the pH was neutral (pH = 7). Then it was heated in an oven at a temperature of 150 °C for 30 min so that activated adsorbent could be obtained. Next, the activated adsorbent was characterized (Sembiring et al., 2021c).

Table 1
Properties of the light naphtha.

Property	value
API	71
Initial boiling point, (°C)	42
Ending boiling point (°C)	130
Reid vapor pressure@37.8 °C	8.5
Sulfur content, (ppm)	776

2.1. *Using Box-Behnken experiment design with response surface methodology* (RSM)

RSM is a statistical technique used for assessing the relation between real experimental results (response) and studied variables (control variables), and this is usually done by combining RSM with factorial design techniques such as central-composite design (CCD) and Box-Behnken design (BBD). The BBD method was helping to reduce the required number of experiments with a high degree of accuracy in the optimization in comparison with other factorial design methods. The required experiment number to cover the studied variable system according to BBD is:

$$N = 2k(k-1) + r \tag{1}$$

Where N is the number of experiments, k is the number of variables, and r is the replicate number of central points (3–6). BBD stated that the levels of the studied variables were adjusted to only three levels (−1.0, 1) with equal values for the interval between each level; thus, for three variables with three levels, the number of experiments was 15–18 depending on the number of replicated experiments (r in the equation). The chosen studied variables are temperature, adsorbent dosage, and contact time with ranges of 20–40 C°, 1–3 g, and 15–45 min, respectively, to investigate the activity of absorbent in the light naphtha ADS process as listed in Table 2, the experimental design with Minitab version 17 as shown in Table 3.

The experiment results for the effects of temperature (x1), adsorbent dosage (x2), and contact time (x3) on ADS were fitted as second-order polynomials, and they can be used to estimate and predict values and optimize the system for three variables where the second-order polynomial is represented by the equation:

$$R\% = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j + \varepsilon \tag{2}$$

Where R% is the predicted response, β0 is the intercept coefficient, βi is the linear effect (slope) of input variable xi, βij is the interaction effect of linear by linear between two input variables xi, and Bii is the squared effect.

2.2. *ADS activity investigation*

Batch adsorption was used to study the activity of the adsorbent. The studied variables were temperature, amount of adsorbent, and contact time, with ranges of 20–40 °C, 1–3 g, and 15–45 min, respectively. The impact of the studied variables was designed according to Box-Behnken's experimental design; this design states that it was necessary to conduct 15 experiments for a three-variable system, as shown in Table 3. 100 ml of light naphtha was put into a conical flask and started heating with continued stirring (300 rpm) while the temperature was adjusted according to the Box-Behnken experimental design matrix. As the temperature reached the adjusted value, the specified adsorbent dosage was poured into the conical flask, and the process was stopped at the end of the required time. To separate the adsorbent from the light naphtha with

Table 2
Independent (controllable) variables and their levels.

variables, unit	symbol coded	Actual	levels −1	0	1
Temperature (°C)	x_1	X_1	20	30	40
Adsorbent dosage (g)	x_2	X_2	1	2	3
Contact time	x_3	X_3	15	30	45

Table 3
Box-Behnken design (BBD) matrixes.

Run	design parameters x_1	x_2	x_3	Run	design parameters x_1	x_2	x_3	Run	design parameters x_1	x_2	x_3
1	1	0	−1	6	0	1	1	11	0	0	0
2	−1	0	1	7	0	−1	−1	12	−1	0	−1
3	1	−1	0	8	0	0	0	13	0	1	0
4	1	1	0	9	0	0	0	14	−1	1	0
5	0	−1	1	10	1	0	1	15	−1	−1	0

a low sulfur content, the mixture underwent filtration. Finally, Oxford Company used X-ray fluorescence to measure the sulfur content in accordance with ASTM D-4294. The sulfur removal percent was calculated by (Kundu and Mitra 2021):

$$R\% = \frac{W_0 - w_f}{W_0} \tag{3}$$

Where w_o is initial amount of sulfur in light naphtha (ppm) and w_f is final amount of sulfur in light naphtha (ppm) respectively.

3. Result and discussion

3.1. Characterization of prepared catalyst

The XRD pattern for prepared adsorbent is shown in Fig. 1, and Table 4 shows the diffraction angles for the adsorbent and comparison with the standard card (JCPDS 85–1180). It can be noted that the activated adsorbent contains calcium carbonate ($CaCO_3$) because the XRD diffractogram shown at an angle of 2θ shows that several peaks produced refer to the diffraction pattern of the JCPDS data (Sembiring et al., 2021b).

The $CaCO_3$ crystal size d_P for as-prepared samples was determined by determining the most intense peak broad according to the Debye-Scherrer equation:

$$d_P = \frac{\kappa\lambda}{\beta cos\theta} \tag{4}$$

Where κ is the correction factor that accounts for particle shape (and it equals 0.94), β is full width at half maximum FWHM, λ is the wavelength of the Cu target (0.1518 Å), and θ is Bragg`s angle (Balakrishnan and John 2020). Table 5 shows the calculated crystallite size according to the equation, in which the 5th column shows the crystal size for all peaks, and the obtained average crystallite size is 7.7 nm. The XRD

Table 4
Data for peak (2θ) for the prepared sample and peak at standard JCPDC card.

Prepared sample Diffraction angle (2θ in degree)	d –spacing (Å)	Standard –JCPDS 85–1108 Diffraction angle (2θ in degree)	d –spacing (Å)
29.381	3.0374	29.466	3.0289
31.417	2.8451	31.516	2.8364
39.42	2.284	39.489	2.2801
43.16	2.0943	43.244	2.0904
47.14	1.9263	47.213	1.9235
48.501	1.8754	48.615	1.8713
56.6	1.6248	56.678	1.6227
57.436	1.6031	57.517	1.6010
60.699	1.5245	60.798	1.5222
64.721	1.4391	64.795	1.4376

Table 5
The structural parameters for prepared sample of calcite.

Diffraction angle (2θ in degree)	FWHM (β) (°)	d –spacing (Å)	Crystal size (d_P) (nm)	Dislocation density (δ) nm^{-2}	Strain (ε) × 10^{-3}
29.381	0.209	3.0374	1.299	0.592627	32.2749
31.417	0.161	2.8451	0.886	1.273892	74,990.86
39.42	0.207	2.284	1.057	0.895056	44.512
43.16	0.205	2.0943	0.759	1.735867	117.547
47.14	0.257	1.9263	68.929	0.00021	51.755
48.501	0.257	1.8754	0.874	1.309113	52.872
56.6	0.145	1.6248	0.984	1.032785	1412.058
57.436	0.254	1.6031	0.622	2.584754	133.609
60.699	0.389	1.5245	0.759	1.735867	53.681
64.721	0.285	1.4391	0.854	1.371148	51.538

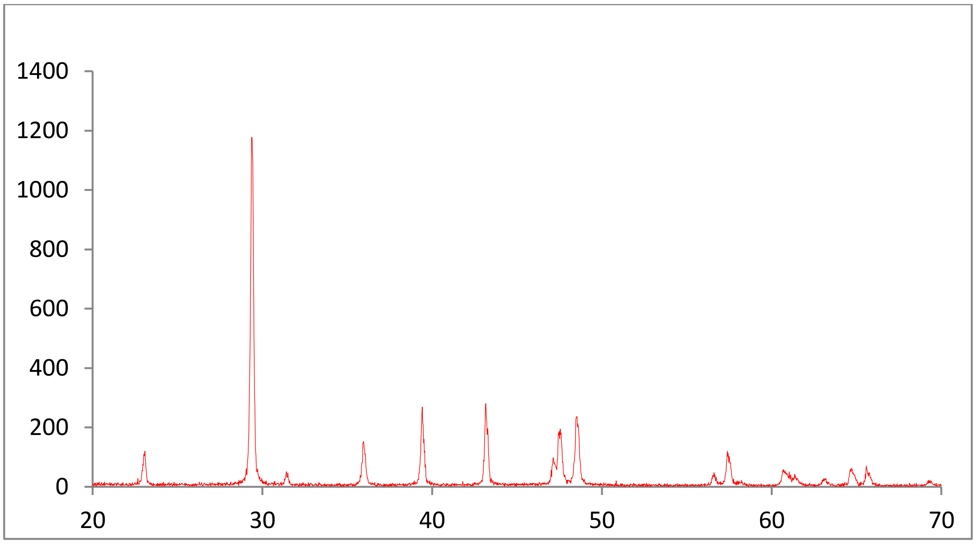

Fig. 1. XRD pattern for prepared calcite as an adsorbent.

pattern and the values for the size of the crystallites show that the size of the crystallites depends on things like peak boarding, intensity, dislocation density, sharpness, and strain. The strain (ε) and the dislocation density (δ) are calculated by using the following equations:

$$\text{Dislocation density } (\delta) = \frac{1}{D^2} \tag{5}$$

$$\text{Strain } (\varepsilon) = \frac{\beta}{(4\cos(\theta))} \tag{6}$$

The variation of dislocation density and crystallite size with respect to strain is shown in Table 5. It clearly shows that the dislocation density increases as strain increases, which in turn decreases the crystallite size. It also confirms that strain and dislocation density are directly influenced by crystallite size (Venkateswarlu et al., 2014),and (San et al., 2022).

Fig. 2 illustrates the FTIR spectra of prepared $CaCO_3$ from eggshell, in which the spectra analysis shows an apparent peak at 711,872, 2516 cm $^{-1}$. A severe peak of eggshell particles is absorbed at 1487 cm^{-1}, which can be strongly associated with the presence of carbonate minerals within the eggshell matrix. The peaks at 3400 and 2516 cm $^{-1}$ may be referred to as the presence of hydroxyl (-OH) groups and acidic hydrogen (-OH) groups. The two peaks noted clearly at about 712 and 872 cm^{-1}, respectively, indicated the presence of calcium carbonate (Tizo et al., 2018; Ahmad et al., 2012). A better understanding of how contaminants interact with and interfere with the $CaCO_3$-based organic membrane under controlled conditions can help in the future with the development of compact, optimal treatment strategies (Ningrum et al., 2022).

3.2. *Adsorptive desulfurization results*

Table 6 shows the adsorptive desulfurization (ADS) by prepared $CaCO_3$ adsorbent for all BBD-designed experiments. The sulfur removal efficiency ranged between 45 and 60%; furthermore, the experiment results were fitted with a second-order polynomial (quadratic model) with Box-Behnken design and Minitab software version 17. The fitting product shows that a regression equation in uncoded variables for using $CaCO_3$ adsorbent is:

$$R\% = 32.6 + 0.688X_1 - 1.08X_2 - 0.014\,X_3 - 0.00167\,X_1^2 + 0.583X_2^2 - 0.00074\,X_3^2 - 0.0250\,X_1X_2 - 0.00000X_1X_3 + 0.0500X_2X_3 \tag{7}$$

As noted from the analysis of variance ANOVA, the F-value is 11.19 for regression, and it was greater than the tabulated value for Fisher`s (*F* = 4.77). The high R^2 (0.9527) with high values for adjusted R^2 (0.8676) indicates that the assumed model is reasonably well fitting with real results; moreover, based on actual results and ANOVA, the temperature has the highest effect on sulfur adsorption, whereas other parameters effects are ordered as follows: adsorbent dosage and adsorption time via their F-values of 86.13, 93, and 1.16 for temperature, adsorbent dosage, and adsorption time, respectively. The sulfur removal efficiency of ADS increased as temperature, adsorbent dosage, and adsorption time increased. The results analysis shows the optimum sulfur removal efficiency is 60% at the following operation conditions: 40 °C, 3 gmes, and 45 min for temperature, adsorbent dosage, and adsorption time, respectively, as shown in Fig. 3. (Table 7)

4. Effect of studied variables on ADS

4.1. *Effect of adsorption dose on desulfurization removal*

The increasing of adsorbent dosage led to increasing in sulfur removal efficiency. The increasing dosage of calcite indicates an increase in the adsorbent's surface area or in another meaning raised the number of adsorption sites on the surface of the adsorbent, thereby enhancing its adsorption capacity (Üçer et al., 2006).

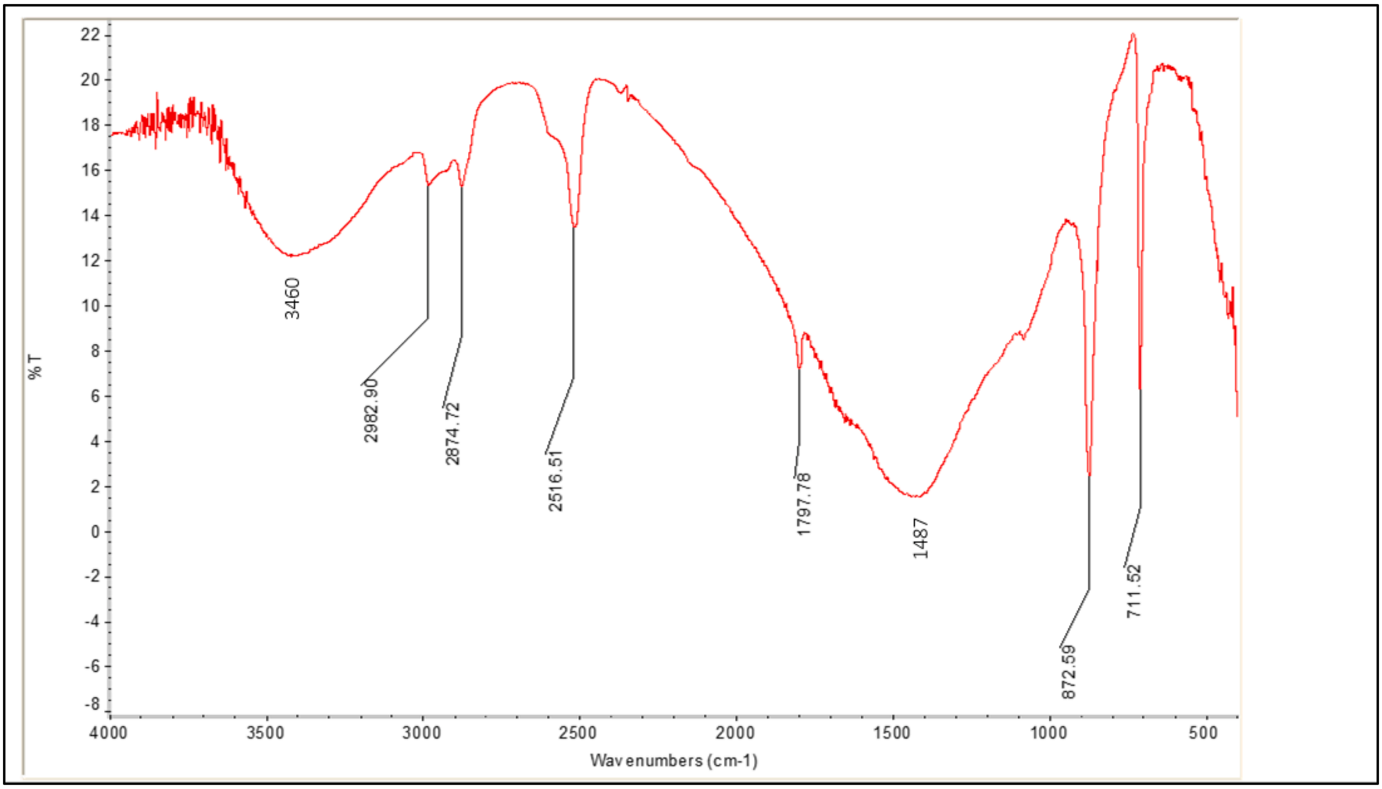

Fig. 2. FTIR spectra for prepared calcite as an adsorbent.

Table 6
Experimental (actual) value for sulfur removing efficiency for all runs.

Run	Temperature	Adsorbent dosage	Time	R%	Run	Temperature	Adsorbent dosage	Time	R%
1	40	2	15	57	9	30	2	30	50
2	20	2	45	47	10	40	2	45	58
3	40	1	30	56	11	30	2	30	55
4	40	3	30	60	12	20	2	15	46
5	30	1	45	51	13	30	3	15	53
6	30	3	45	56	14	20	3	30	50
7	30	1	15	51	15	20	1	30	45
8	30	2	30	52					

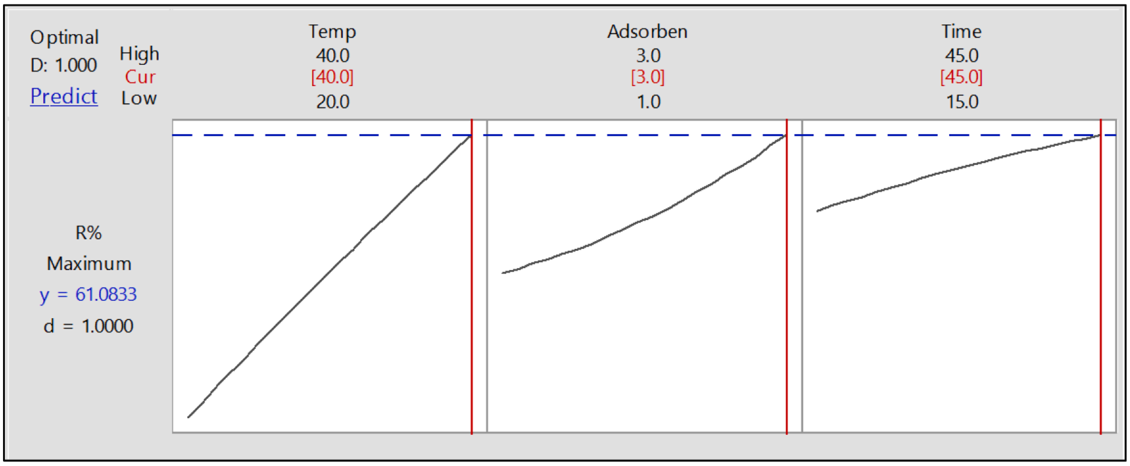

Fig. 3. Optimum conditions for light naphtha ADS process with calcite adsorbent; 40 °C, 3 gs and 45 min for temperature, adsorbent dosage, and adsorption time respectively, also the figure show the general effect of studied variables on sulfur removing efficiency as temperature, adsorbent dosage, and adsorption time increasing.

Table 7
ANOVA analysis results for RSM for quadratic model.

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	9	270.317	30.035	11.19	0.008
Linear	3	266.250	88.750	33.07	0.001
Temp (X_1)	1	231.125	231.125	86.13	0.000
Adsorbent dosage (X_2)	1	32.000	32.000	11.93	0.018
Time (X_3)	1	3.125	3.125	1.16	0.330
Square	3	1.567	0.522	0.19	0.896
Temp*Temp (X_1) ^{2}	1	0.103	0.103	0.04	0.853
Adsorbent dosage*Adsorbent dosage (X_2)^2	1	1.256	1.256	0.47	0.524
Time*Time (X_2) $_2$	1	0.103	0.103	0.04	0.853
2-Way Interaction	3	2.500	0.833	0.31	0.818
Temp*Adsorbent dosage (X_1) (X_2)	1	0.250	0.250	0.09	0.772
Temp*Time (X_1) (X_3)	1	0.000	0.000	0.00	1.000
Adsorbent dosage*Time (X_2) (X_3)	1	2.250	2.250	0.84	0.402

4.2. *Effect temperatures on desulfurization removal*

The results demonstrated that when the system temperature was increased, the percentage desulfurization efficiency also increased. Higher temperatures accelerate light naphtha spread across the external borders and internal pores within the adsorbent material. So, at increasing temperature, which increases mobility and reduces the viscosity of large OSCs molecules, thereby producing a swelling effect within the internal structure of the adsorbent (Abdus-Salam et al., 2016).

4.3. *Effect of contact time on desulfurization removal*

The percentage desulfurization efficiency improved as the desulfurization time for sulfur in light naphtha increased. This could be because it is common knowledge that the sulfur content of a solution will be better treated thermally or in contact with surface area adsorbents for a longer period if the time of desulfurization is increased relative to the time spent desulfurizing the solution. Therefore, the adsorbent has a greater capacity for sulfur conversion or adsorption. Therefore, the efficiency of light naphtha desulfurization will be increased.(Mohammmed Nsaif Abbas and Ibrahim 2020b).

Figs. 4-6 show the contour chart, which illustrates the interaction effect of each of the two variables on sulfur removal efficiency. As it was shown when studying the individual effect of each variable, the removal efficiency increases with the increase of the variables.

4.4. *Adsorption isotherm*

To analyze the interaction between the adsorbate and the adsorbent, the experimental data of the adsorption process were fitted to Langmuir, Freundlich, Dubinin, Radushkevich and Temkin isotherm models (Kundu and Mitra 2022a). The interaction between adsorbate and adsorbent was described as adsorption isotherms, and they are important to optimize the usage of any adsorbent. The profile of the isotherm provides information about the stability of the interaction and the adsorption convergence of molecules. Some of these adsorption isotherms may be characterized in many mathematical forms, which are based on the streamlined physical behavior of adsorption, whereas the others are empirical and correlated experimental results. Langmuir and Freundlich isotherms were verified for batch results in which the Langmuir and Freundlich isotherm models are used to explain the adsorption equilibrium. The adsorbent capacity was calculated as

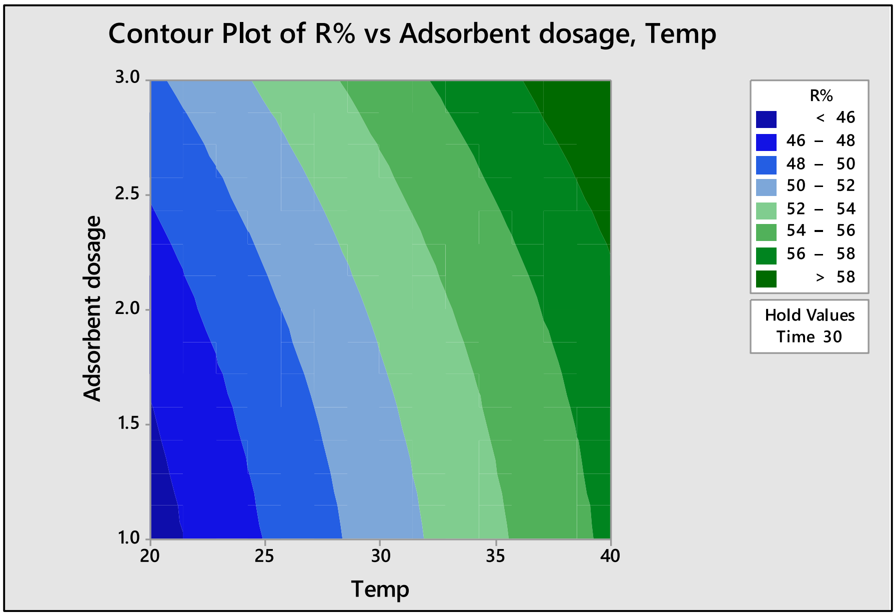

Fig. 4. The interaction effect of temperature and adsorbent dosage on sulfur removal efficiency while kept adsorption time at 30 min.

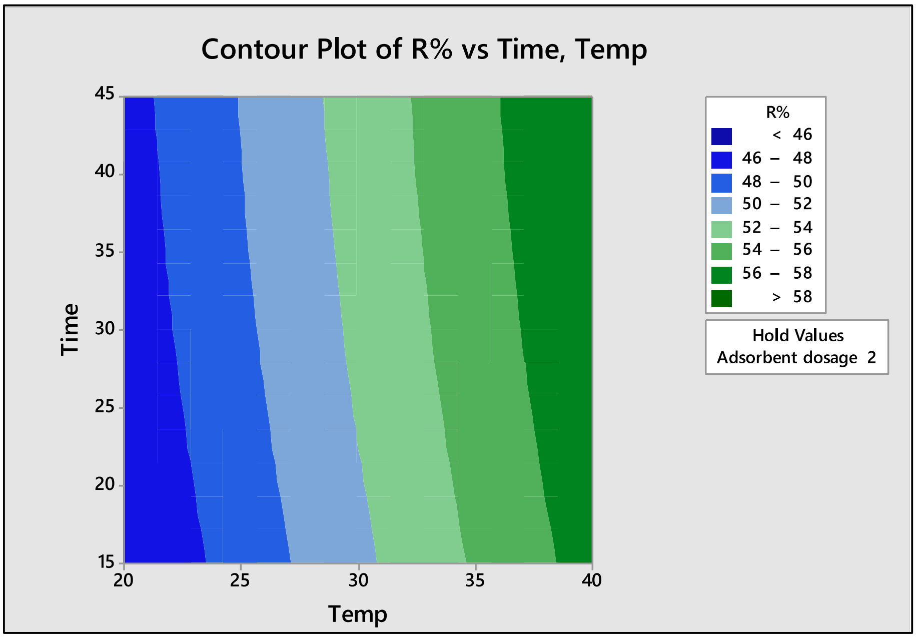

Fig. 5. The interaction effect of temperature and adsorption time on sulfur removal efficiency while kept adsorption dosage 2 g.

follows (Kundu and Mitra 2022b):

$$q = \frac{(C_0 - C_e)V}{w} \tag{8}$$

where q (mg/g) is the amount of absorbate absorbed (mg) divided by the amount of absorbent (g). Ce and C_0 are the initial and equilibrium concentrations of SOCs (mg/L), V is the solution volume (L), and w is the adsorbent weight (g). The amount of SOCs adsorbed, qe (mg/g), per gramme of adsorbent (calcite), was studied. The adsorption isotherm can explain the adsorption capacity at different equilibrium concentrations. Adsorption isotherm for SOCs on calcite at different temperatures (20, 30, and 40 °C). As is well known, the adsorption process may be described by the Langmuir and the Freundlich isotherms. Fig. 7 shows the Langmuir isotherm at different temperatures. The Langmuir isotherm postulates that no more adsorptions can occur at that site if SOCs occupy the sites on the adsorbent's surface. Mathematically, the Langmuir equation can be expressed as follows (Azimi et al., 2017):

$$q_e = \frac{q_{\max K_L C_e}}{1 + K_l C_e} \tag{9}$$

In linear form is:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}} \tag{10}$$

Here qmax is the amount of adsorbate in the case of complete monolayer coverage (mg/g), and K_L is the Langmuir adsorption constant (L/mg), which is related to adsorption free energy. The constants K_L and qmax can be estimated from the intercepts and slops of straight lines in plots of Ce/qe versus Ce.

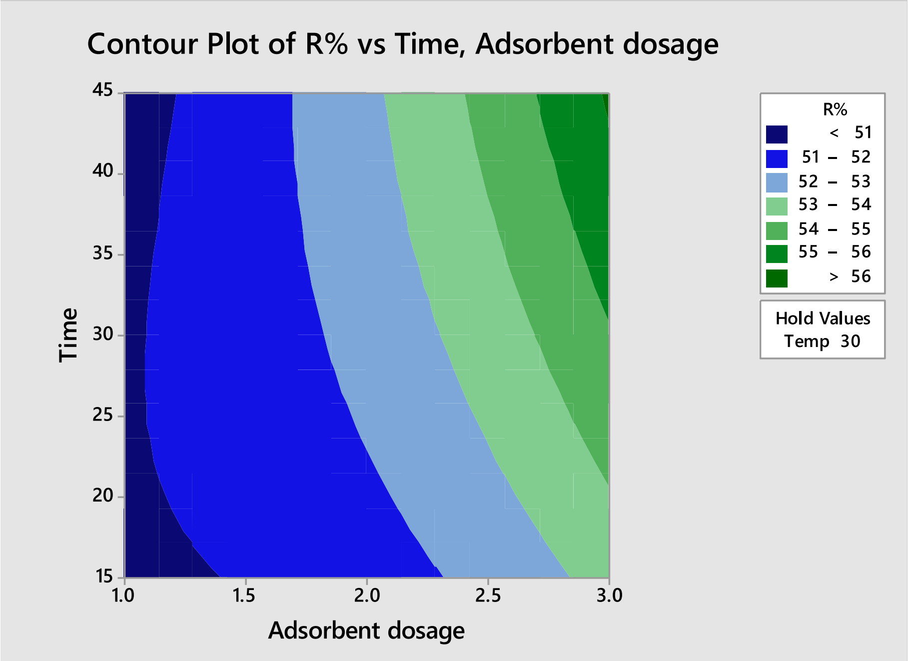

Fig. 6. The interaction effect of adsorption time and adsorbent dosage on sulfur removal efficiency while kept temperature at 30 °C.

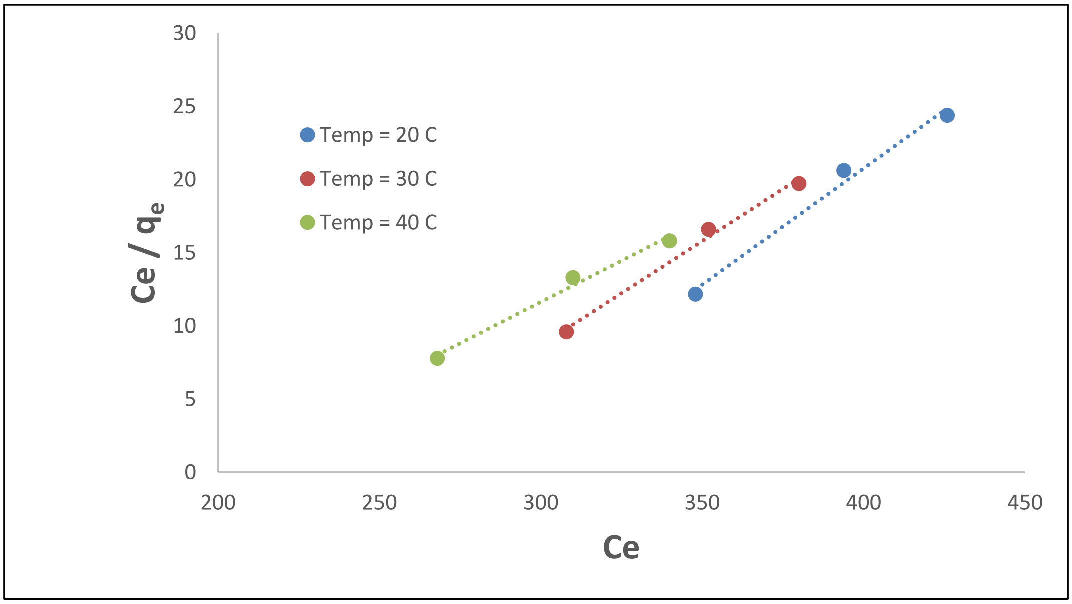

Fig. 7. Langmuir isotherm for OSCs adsorption onto calcite adsorbent at different tempertures.

The Freundlich isotherm can be seen in Fig. 8, where the Freundlich equation is an experimental equation with the following form:

$$q_e = K_F C_e^{1/n} \tag{11}$$

In linear form, it is:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{12}$$

Where qe is the solid phase adsorbate concentration at equilibrium (mg/g) and Ce is the liquid phase concentration at equilibrium (mg/L), K_F is the Freundlich constant [(mg/g)(L/mg) 1/n] and (1/n) is the heterogeneity factor. The constants K_F and exponent (1/n) can be determined from the intercepts and slops of straight lines in the plots in Fig. 8.

From Table 8, the experimental data on the adsorption of sulfur compounds on calcite as an adsorbent have a negative slope when represented by the Langmuir model. This case may occur when the constants are calculated in a too steep experimental part. It is suggested that the adsorption behavior of the tested systems does not favor the assumption of the Langmuir model even though its correlation coefficient is the closest to unity; therefore, the Freundlich isotherm is more suitable to describe the adsorption of these sulfur compounds within the given concentration range (Shikuku et al., 2018).

5. Conclusion

Sulfur is the most hazardous element associated with transportation fuel, which causes pollution after combustion via SOx emissions, causing

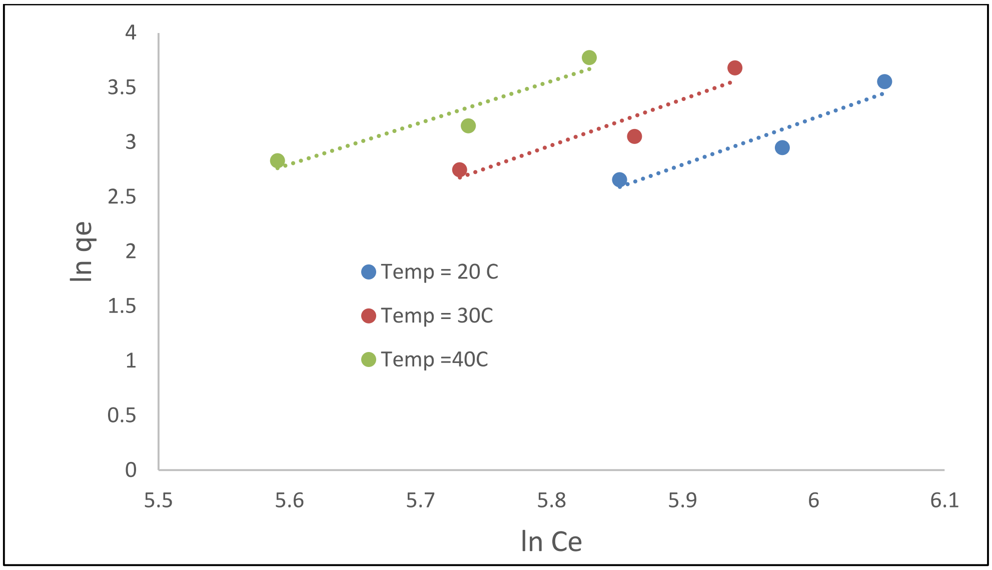

Fig. 8. Freundlich isotherm for OSCs adsorption onto calcite adsorbent at different tempertures.

Table 8
Langmuir and Freundlich model parameters.

Temp.(°C)	Langmuir constants q $_{max.}$(mg/ g)	K_L (L/ mg)	R^2	Freundlich constants K_F [(mg/g) (L/mg) $^{1}/_{n}$]	n	R^2
20	−6.60	-1.94×10^{-3}	0.9002	2.15×10^{-10}	0.235	0.895
30	−7.42	-2.17×10^{-3}	0.886	5.31×10^{-10}	0.238	0.8824
40	−9.24	-2.38×10^{-3}	0.9085	8.66×10^{-9}	0.262	0.9047

acid rain and severe toxic effects on human health. In fuel cell applications, sulfur poisons the catalysts of the fuel processor and the electrodes in the fuel cell stack, causing rapid degradation. This work is an attempt to examine a cheap and green adsorbent for adsorptive desulfurization; this adsorbent is calcite prepared from chicken eggshell. The results show that the sulfur-removing efficacy ranged between 45 and 60%, while optimum sulfur removal efficiency is 61% at the following operation conditions: 40 °C, 3 gmes, and 45 min for temperature, adsorbent dosage, and adsorption time respectively. Adsorption isotherms Langmuir and Freundlich were examined, and the results show the Freundlich isotherm is more suitable to describe the adsorption of these sulfur compounds. The results showed that the used calcite adsorbent has a promising effect towards desulfurization, and there may be a need for making some modifications to the calcite adsorbent to improve the specifications that would boost desulfurization.

Declaration of Competing Interest

The authors whose names are listed immediately below certify that they have NO affiliations with or involvement in any organization or entity with any financial interest (such as honoraria; educational grants; participation in speakers' bureaus; membership, employment, consultancies, stock ownership, or other equity interest; and expert testimony or patent-licensing arrangements), or non-financial interest (such as personal or professional relationships, affiliations, knowledge or beliefs) in the subject matter or materials discussed in this manuscript.

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Please specify the nature of the conflict on a separate sheet of paper if the space below is inadequate.

References

Abbas, Mohammad N, Alalwan, Hayder A, 2019. Catalytic Oxidative and Adsorptive Desulfurization of Heavy Naphtha Fraction. Hwahak Konghak 57 (2), 283–288.

Abbas, Mohammmed Nsaif, Ibrahim, Suha Anwer, 2020a. Catalytic and Thermal Desulfurization of Light Naphtha Fraction. J. King Saud Univ.-Eng. Sci. 32 (4), 229–235.

Abbas, Mohammmed Nsaif, Ibrahim, Suha Anwer, 2020b. Catalytic and Thermal Desulfurization of Light Naphtha Fraction. J. King Saud Univ.-Eng. Sci. 32 (4), 229–235.

Abdus-Salam, Nasir, Magaji, Buhari, Salam, Nasiru Abdus, Buhari, Magaji, Abdus-Salam, Nasiru, 2016. Adsorption of Alizarin and Fluorescein Dyes onto Palm Seeds Activated Carbon: Kinetic and Thermodynamic Studies. J. Chem. Soc. Pak. 38. https://www.researchgate.net/publication/309667414.

Ahmad, Mahtab, Usman, Adel R A, Lee, Sang Soo, Kim, Sung-Chul, Joo, Jin-Ho, Yang, Jae E, Ok, Yong Sik, 2012. Eggshell and Coral Wastes as Low Cost Sorbents for the Removal of Pb2+, Cd2+ and Cu2+ from Aqueous Solutions. J. Ind. Eng. Chem. 18 (1), 198–204.

Ataman, E., Andersson, M.P., Ceccato, M., Bovet, N., Stipp, S.L.S., 2016. Functional Group Adsorption on Calcite: II. Nitrogen and Sulfur Containing Organic Molecules. J. Phys. Chem. C 120 (30), 16597–16607. https://doi.org/10.1021/acs.jpcc.6b01359.

Azimi, Arezoo, Azari, Ahmad, Rezakazemi, Mashallah, Ansarpour, Meisam, 2017. Removal of Heavy Metals from Industrial Wastewaters: A Review. ChemBioEng Rev. 4 (1), 37–59.

Bakr, Abu, Salem, S.H., 1994. Naphtha Desulfurization by Adsorption. Ind. Eng. Chem. Res. 33.

Balakrishnan, Manikandan, John, Rita, 2020. Properties of Sol-Gel Synthesized Multiphase TiO2 (AB)-ZnO (ZW) Semiconductor Nanostructure: An Effective Catalyst for Methylene Blue Dye Degradation. Iran. J. Catal. 10 (1), 1–16.

Chen, Kun, Li, Weining, Biney, Bernard Wiafe, Li, Zhuo, Shen, Jiahua, Wang, Zongxian, 2020. Evaluation of Adsorptive Desulfurization Performance and Economic Applicability Comparison of Activated Carbons Prepared from Various Carbon Sources. RSC Adv. 10 (66), 40329–40340. https://doi.org/10.1039/d0ra07862j.

Elkady, M.F., Ibrahim, Amal M, El-Latif, M M Abd, 2011. Assessment of the Adsorption Kinetics, Equilibrium and Thermodynamic for the Potential Removal of Reactive Red Dye Using Eggshell Biocomposite Beads. Desalination 278 (1–3), 412–423.

Hussein, Ali A, Fadhil, Abdelrahman B, 2021. Kinetics and Isothermal Evaluations of Adsorptive Desulfurization of Dibenzothiophene over Mixed Bio-Wastes Derived Activated Carbon. Energy Sources Part A 1–20.

Ishaq, Muhammad, Sultan, Siraj, Ahmad, Imtiaz, Ullah, Hameed, Yaseen, Muhammad, Amir, Alia, 2017. Adsorptive Desulfurization of Model Oil Using Untreated, Acid Activated and Magnetite Nanoparticle Loaded Bentonite as Adsorbent. J. Saudi Chem. Soc. 21 (2), 143–151. https://doi.org/10.1016/j.jscs.2015.02.003.

Jha, Divyam, Belal Haider, Mohd, Kumar, Rakesh, Shim, Wang Geun, Sivagnanam, Balathanigaimani Marriyappan, 2020. Batch and Continuous Adsorptive Desulfurization of Model Diesel Fuels Using Graphene Nanoplatelets. J. Chem. Eng. Data 65 (4), 2120–2132.

Kadhum, Ammar T, Albayati, Talib M, 2022. Desulfurization Techniques Process and Future Challenges for Commercial of Crude Oil Products. In: AIP Conference Proceedings, 2443. AIP Publishing LLC, 030039.

Kundu, Subhajit, Mitra, Debarati, 2021. Non-Catalytic Desulfurization of Model Diesel Using Synthesized Biodegradable Ionic Liquid. Energ. Sourc. Part A: Recov. Utiliz. Environ. Effects. https://doi.org/10.1080/15567036.2021.1966137.

Kundu, Subhajit, Mitra, Debarati, 2022a. Immobilization of Acetate Based Ionic Liquids on Silica Gel to Fabricate a Prospective Desulfurizing Adsorbent. Soft Mater. 20 (3), 344–357. https://doi.org/10.1080/1539445X.2022.2049307.

Kundu, Subhajit, Mitra, Debarati, 2022b. Studies on Adsorption Isotherm and Adsorption Kinetics to Predict the Behavior of an Ionic Liquid Based Adsorbent in Desulfurization of Model Diesel. Russ. J. Appl. Chem. 95 (8), 1207–1217. https://doi.org/10.1134/S1070427222080171.

Mohammed, Mohammed Y, Al-Bayati, Talib M, Ali, Alaa Mashjel, 2022. The Role of Extractive and Oxidative Desulphurization Techniques of Fuel Oils Using Ionic Liquids: An Overview. In: AIP Conference Proceedings, 2443. AIP Publishing LLC, 030026.

Naife, Tariq Mohammed, Finish, Qusay Ghanim, 2021. Adsorption Desulfurization of Iraqi Light Naphtha Using Metals Modified Activated Carbon. J. Eng. 27 (7).

Ningrum, R.A., Humaidi, S., Sihotang, S., Bonardo, D., 2022. Synthesis and Material Characterization of Calcium Carbonate (CaCO3) from the Waste of Chicken Eggshells. In: Journal of Physics: Conference Series, 2193. IOP Publishing, 012009.

Saleh, Tawfik A, Danmaliki, Gaddafi I, Shuaib, Taye Damola, 2016. Nanocomposites and Hybrid Materials for Adsorptive Desulfurization. Applying Nanotechnology to the Desulfurization Process in Petroleum Engineering. IGI Global, pp. 129–153.

San, Xingyuan, Gong, Mingyu, Wang, Jian, Ma, Xiuliang, Reis, Roberto dos, Smeets, Paul J M, Dravid, Vinayak P, Hu, Xiaobing, 2022. Uncovering the Crystal Defects within Aragonite CaCO3. Proc. Natl. Acad. Sci. 119 (14), e2122218119.

Sembiring, Helmina Br, Pasaribu, Nurhaida, Sitepu, Josua, 2021a. Calcium Carbonate from Chicken Eggshells as Adsorbents. In: AIP Conference Proceedings, 2342. AIP Publishing LLC, 070005.

Sembiring, Helmina Br, Pasaribu, Nurhaida, Sitepu, Josua, 2021b. Calcium Carbonate from Chicken Eggshells as Adsorbents. In: AIP Conference Proceedings, 2342. AIP Publishing LLC, 070005.

Sembiring, Helmina Br, Pasaribu, Nurhaida, Sitepu, Josua, 2021c. Calcium Carbonate from Chicken Eggshells as Adsorbents. In: AIP Conference Proceedings, 2342. American Institute of Physics Inc. https://doi.org/10.1063/5.0046388.

Shikuku, Victor O, Zanella, Renato, Kowenje, Chrispin O, Donato, Filipe F, Bandeira, Nelson M G, Prestes, Osmar D, 2018. Single and Binary Adsorption of Sulfonamide Antibiotics onto Iron-Modified Clay: Linear and Nonlinear Isotherms, Kinetics, Thermodynamics, and Mechanistic Studies. Appl. Water Sci. 8, 1–12.

Srivastav, Ankur, Srivastava, Vimal Chandra, 2009. Adsorptive Desulfurization by Activated Alumina. J. Hazard. Mater. 170 (2–3), 1133–1140. https://doi.org/10.1016/j.jhazmat.2009.05.088.

Srivastava, Vimal Chandra, 2012. An Evaluation of Desulfurization Technologies for Sulfur Removal from Liquid Fuels. RSC Adv. 2 (3), 759–783.

Tizo, Maribel S, Blanco, Lou Andre V, Cagas, Andrian Cris Q, Cruz, Buenos Rangel B Dela, Encoy, Jimrey C, Gunting, Jemalyn V, Arazo, Renato O, Mabayo, Val Irvin F, 2018. Efficiency of Calcium Carbonate from Eggshells as an Adsorbent for Cadmium Removal in Aqueous Solution. Sustain. Environ. Res. 28 (6), 326–332.

Üçer, A., Uyanik, A., Aygün, Ş.F., 2006. Adsorption of Cu (II), Cd (II), Zn (II), Mn (II) and Fe (III) Ions by Tannic Acid Immobilised Activated Carbon. Sep. Purif. Technol. 47 (3), 113–118.

Venkateswarlu, K., Sandhyarani, M., Nellaippan, T.A., Rameshbabu, N., 2014. Estimation of Crystallite Size, Lattice Strain and Dislocation Density of Nanocrystalline Carbonate Substituted Hydroxyapatite by X-Ray Peak Variance Analysis. Procedia Mater. Sci. 5, 212–221. https://doi.org/10.1016/j.mspro.2014.07.260.